

# Observation of the $A^2\Delta$ - $X^2\Pi$ transition spectra of CD molecules under a magnetic field relevant to fusion plasmas

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## Abstract

The CD  $A^2\Delta - X^2\Pi$  transition spectra under an external magnetic field are calculated based on quantum mechanical perturbation method, and the results are compared with measurements in glow-discharge plasmas. The values of the equilibrium molecular constants,  $T_e$ ,  $\omega_e$ , and  $B_e$  for the  $A^2\Delta$  state, are determined from the comparison of the spectra under no magnetic field. The measured spectra under a field strength up to 4.0 T are well reproduced by the calculation using these molecular constants.

*Keywords:*

plasma, plasma spectroscopy, diatomic molecule, Zeeman effect, hydrocarbon, CD, molecular constants

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## 1. Introduction

In magnetic confinement fusion experiments, accurate modeling of the generation and transport of hydrocarbon molecules is an issue to predict the formation of the carbon-tritium co-deposition layer and resultant amount of tritium inventory in devices which implement carbon plasma facing components[1]. The accumulation of experimental data in terms of chemical sputtering yield

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and  $D/XB$  ratio under various experimental conditions is therefore necessary. The deduction of hydrocarbon molecular flux is based on visible optical emission spectroscopy of the CH (and its hydrogen isotopomers CD and CT)  $A^2\Delta - X^2\Pi$  and  $C_2$   $d^3\Pi_g - a^3\Pi_u$  transition spectra[2, 3, 4, 5]. To evaluate the total intensity, there has been adopted integration of the emission intensity in a certain wavelength range near the bandhead. This procedure is applicable under a condition of no line blending in the corresponding wavelength region, but otherwise the application may cause an error in evaluated intensity. In particular, in plasmas containing mixed hydrogen isotopes, the spectra of CH isotopomers can be partially overlapped because these spectra have a close wavelength. A solution to overcome this difficulty is detailed modeling of ro-vibronic structures in the spectra[6, 7, 8, 5]. This approach is effective not only to separate the isotope spectra but also to remove ambiguity in the evaluation of the emission intensity by quantifying the ro-vibronic excitation population distributions. Moreover, one may be able to obtain additional information about the spatial distribution of the emission intensity from the observed Zeeman splitting in the spectra[9].

In our previous paper[5], we calculated the  $Q$ -branch spectra of the CH  $A^2\Delta - X^2\Pi$  transition under external magnetic fields, and verified the results by basic experiments carried out using a glow-discharge plasma installed in a superconducting magnet. In this paper, we extend the method to the CD spectra. Calculation of the CD spectra requires more elaboration than that of the CH spectra because of deficiency in the accurate values of the molecular constants for the upper  $A^2\Delta$  state. Values of some molecular constants are thus determined from a comparison between calculation and experiment.

## 2. Calculation of the CD $A^2\Delta - X^2\Pi$ transition spectra

The CD  $A^2\Delta - X^2\Pi$  transition spectra under an external magnetic field were calculated based on quantum mechanical perturbation theory utilizing the effective Hamiltonian. Details of the method are summarized in a previous paper[5], so that here we mention briefly. We adopted a total Hamiltonian  $H_{\text{tot}}$  in the presence of an external magnetic field as follows:

$$H_{\text{tot}} = H_{\text{ele}} + H_{\text{vib}} + H_{\text{rot}} + H_{\text{cd}} + H_{\text{so}} + H_{\text{sr}} + H_{\text{ld}} + H_{\text{B}}, \quad (1)$$

where the terms on the right-hand side represent the ro-vibronic energies, centrifugal distortion, spin-orbit interaction, spin-rotation interaction,  $\Lambda$ -type

doubling, and Zeeman effect, respectively. The matrix elements were calculated using Hund's case (b) wave function. The ro-vibronic emission intensities were calculated within the Born-Oppenheimer approximation, and the ro-vibrational population density of the  $A^2\Delta$  state was assumed to be in the Boltzmann distribution with single vibrational and rotational temperatures.

### 3. Experiments

Two kinds of experiments were carried out. In the first experiment, we aimed at determining the molecular constants of the  $A^2\Delta$  state. A commercial ac glow discharge lamp (Electro-Technic Products Spectrum Tube) was used with replacing the enclosed gas by pure deuterated methane ( $CD_4$ ) of 200 Pa, which was measured by a capacitance manometer. Emission of the lamp was collected by an achromatic lens and injected into a Czerny-Turner type spectrometer (Jobin-Yvon THR1500;  $f = 1.5$  m, 2400 grooves/mm grating), and the spectrum was recorded by a CCD (Andor DU940-BU2;  $2048 \times 512$  pixels,  $13.5 \mu\text{m}$  square pixel) with an exposure time of 900 s. The spectrometer was operated with an entrance slit width of  $100 \mu\text{m}$  under double-pass mode in which the injected light is dispersed twice before ejection.

The second experiment was conducted to observe magnetic field effects on the spectra. A glow discharge tube installed in a bore of a cryogen free superconducting magnet (Cryogenic 1721) was used. A schematic drawing of the experimental apparatuses is shown in Fig 1. The magnet has bores in directions parallel ( $\phi$  70 mm) and perpendicular ( $\phi$  30 mm) to the field direction. The inhomogeneity of the field strength at the center of the discharge tube is less than 0.25% over a 10-mm-diameter sphere. The discharge tube is made of quartz glass with an inner diameter of 5 mm and a length of 190 mm. The tube was filled with pure  $CD_4$ , and pressure measured by a capacitance manometer was 200 Pa. A dc glow discharge was sustained between hollow-shaped tungsten electrodes, and the discharge voltage and current were about 1 kV and 2.5 mA, respectively. Emission from the positive column was collected in the Voigt configuration using a polarization separation optics (PSO) consisted of a Glan-Taylor prism and quartz lens. Compared to our previous work[5], an additional achromatic lens was installed in the bore to increase the solid angle of the collection. The  $\pi$  and  $\sigma$  components of the emission were measured sequentially by rotating the PSO. The collected emission was transferred via a quartz optical fiber to a Czerny-

Turner type spectrometer (JASCO CT-100CP;  $f = 1.0$  m, 3600 grooves/mm grating), and the spectrum was detected by a liquid nitrogen cooled CCD (Roper Scientific CCD-1100PB;  $1100 \times 300$  pixels,  $24 \mu\text{m}$  square pixel) with an exposure time of 600 s. The entrance slit width was set to  $50 \mu\text{m}$ .

The absolute wavelengths of the spectra were calibrated using ArI (430.0101 nm[15]) and ArII (430.06493 and 430.92385 nm[15]) spectra from a hollow-cathode ThAr glow discharge lamp (Photron Lamps P858A). The reciprocal linear dispersions evaluated from these spectra under an assumption of linear increase in the wavelength with the pixel position were 112 and 141 pm/mm for the first and second experiments, respectively. Assuming that the reference spectra have no wavelength shift by the Doppler or Stark effect, errors in the calibrated wavelength are about 0.2 and 0.9 pm, respectively. These values were estimated from the standard deviations of the fitting coefficients for the reciprocal linear dispersions. The instrumental widths were estimated from the broadening of the CD spectra. After deconvoluting the Doppler broadening with a postulation that the translational temperature equals to the rotational temperature, the widths were 3.7 and 9.7 pm (FWHM), respectively. For all the measured CD spectra, the integrated emission intensities from 430.70 to 430.85 nm were normalized to unity. In the observed wavelength range, several spectra of  $\text{D}_2$  molecules were superposed. Some of them are attributable to the  $I^1\Pi_g-B^1\Sigma_u^+$ ,  $v' - v'' = 1 - 0$  transition[16], where  $v$  is the vibrational quantum number, and prime and double-prime denote the upper and lower states, respectively. Two lines with relatively large intensities at 430.63 and 430.89 nm are identified as  $Q3$  and  $Q2$  transitions, respectively. The wavelengths of the  $\text{D}_2$  transitions were determined experimentally using a commercial  $\text{D}_2$  ac glow discharge lamp (Electro-Technic Products Spectrum Tube).

#### 4. Determination of the ro-vibronic molecular constants for the $A^2\Delta$ state

The observed  $Q$ -branch spectra of the CD  $A^2\Delta-X^2\Pi$  transition in the first experiment is shown in Fig. 2 with the lines and markers. The spectra have a bandhead wavelength of about 430.9 nm and a transition with a larger rotational quantum number has a shorter wavelength. In the calculation of the spectra, vibrationally diagonal transitions up to  $v = 2$  were included. We adopted experimentally evaluated values of the equilibrium molecular constants for the  $X^2\Pi$  state[10]. On the other hand, for the

$A^2\Delta$  state, no accurate data has been compiled since the pioneering work by Gerö[11] to the best of our knowledge. We therefore evaluated the values from those of CH[12] using the isotopic relationships under the Born-Oppenheimer approximation[13, 14]. The scaled values of the equilibrium constants related to the ro-vibronic energies are listed in Tab. 1. The ro-vibronic energies are approximated as follows:

$$\begin{aligned}
E(v, N) &= T_e + G(v) + F(v, N) + \dots, \\
G(v) &= \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + \omega_e y_e \left( v + \frac{1}{2} \right)^3 + \dots, \\
F(v, N) &= B_v N(N+1) - D_v N^2(N+1)^2 + \dots, \\
B_v &= B_e - \alpha_e \left( v + \frac{1}{2} \right) + \gamma_e \left( v + \frac{1}{2} \right)^2 + \epsilon_e \left( v + \frac{1}{2} \right)^3 + \dots, \\
D_v &= D_e + \beta_e \left( v + \frac{1}{2} \right) + \delta_e \left( v + \frac{1}{2} \right)^2 + \zeta_e \left( v + \frac{1}{2} \right)^3 + \dots,
\end{aligned}$$

where  $N$  is the rotational quantum number,  $E(v, N)$  is the total energy,  $T_e$  is the electronic energy,  $G(v)$  is the vibrational energy,  $F(N, v)$  is the rotational energy,  $\omega_e$ ,  $\omega_e x_e$ ,  $\omega_e y_e$ ,  $B_v$ ,  $D_v$ ,  $B_e$ ,  $\alpha_e$ ,  $\gamma_e$ ,  $\epsilon_e$ ,  $D_e$ ,  $\beta_e$ ,  $\delta_e$ , and  $\zeta_e$  are the equilibrium molecular constants. Differences between the scaled and measured data of the first-order constants  $\omega_e$  and  $B_e$  are reported to be less than 0.2% for the CD  $X^2\Pi$  state[10], and this may be similar for the  $A^2\Delta$  state. However, calculated spectra using the scaled constants significantly deviate from the experimental one in particular for transitions with large  $N$  because slight errors in the constants are magnified. To obtain better agreement between the experiment and calculation, we evaluated the values of  $\omega_e$  and  $B_e$ . The calculated spectrum was fitted to the experimental one by varying the emission intensity and wavelength at the bandhead, ro-vibrational temperatures in the  $A^2\Delta$  state, broadening (Gaussian), and zero level besides these molecular constants. The value of  $T_e$  can be calculated from the wavelength at the bandhead. The simultaneous evaluation of the higher-order constants is difficult with the present wavelength resolution, so that these values were fixed to the scaled ones. In the calculation of the relative transition intensities, the Franck-Condon factors were assumed to be equal to those of the CH  $A^2\Delta - X^2\Pi$  transition[12].

The fitting result is shown in Fig. 2 with the dashed line. To avoid the superposition of the  $D_2$  spectra, the fitting was carried out in a wavelength

range 430.3589-430.8758 nm with excluding 430.3785-430.4057, 430.4979-430.5282 and 430.5992-430.6566 nm. The fitting range corresponds to  $N \leq 12$  for the  $v' - v'' = 0 - 0$  transition. The excluded ranges are marked with the horizontal bars at the bottom. These ranges were determined such that the intensities of the D<sub>2</sub> spectra decrease sufficiently smaller than those of the CD spectra. The wavelengths of the ro-vibronic transitions of CD are indicated by the vertical ticks together with those of D<sub>2</sub>. With the present wavelength resolution, the spectra represent the envelope of the overlapped ro-vibronic transitions. The evaluated values of the constants  $T_e$ ,  $\omega_e$ , and  $B_e$  are shown in Tab. 1. The precision of the absolute wavelength is about 0.2 pm, and this equivalents to about  $1 \times 10^{-2} \text{ cm}^{-1}$  at 430 nm. The error in  $T_e$  is determined by this value and the standard deviation of the fitting result. Meanwhile, for  $\omega_e$  and  $B_e$ , the errors are determined by the standard deviations of the fitting results. It should be mentioned that changes in the evaluated values of the molecular constants are smaller than their error bars when we change the short wavelength side of the fitting range below 430.45 nm. The vibrational and rotational temperatures deduced from the fitting are  $T_{\text{vib}} = 2200 \text{ K}$  and  $T_{\text{rot}} = 680 \text{ K}$ , respectively.

## 5. Observation of magnetic field effects on the spectra

A spectrum without the magnetic field was measured again in the second experiment to determine the ro-vibrational temperatures. The measured spectrum and the fitting result are shown in Fig. 3(a). The fitting was carried out in a wavelength range 430.454-430.852 nm using the values of the molecular constants determined above. The fitting range corresponds to  $N \leq 11$  for the  $v' - v'' = 0 - 0$  transition. Wavelength ranges of 430.501-430.524 and 430.609-430.650 nm were excluded from the fitting. A slight disagreement is observed in the spectrum around 430.73 nm. This should be due to the blending of other transition lines since it is not observed in the first experiment. The deduced vibrational and rotational temperatures are  $T_{\text{vib}} = 2900 \text{ K}$  and  $T_{\text{rot}} = 740 \text{ K}$ , respectively. The difference in the temperatures from the first experiment may be originated from differences in discharge method and plasma parameters.

The  $\pi$  and  $\sigma$  polarization components of the spectra measured under magnetic field strengths of 1.5, 4.0, and 7.0 T are shown in Figs. 3(b) and (c), respectively. In the figures, the zero levels of the spectra for the cases of 4.0 and 7.0 T are shifted vertically for better visibility. The magnitude

of wavelength shift by the Zeeman effect is approximately proportional to  $N^{-2}$ [9], and this feature results in salient changes in the shapes of the spectra near the rotational bandheads. For the calculated spectra, the values of the fitting parameters obtained under no magnetic field were used except for the emission intensity of the bandhead and zero level. The fittings were conducted in 430.70-430.85 nm, where the superposition of the D<sub>2</sub> spectra can be neglected. For the cases of 1.5 and 4.0 T, the agreements of the calculated and observed spectra for both the  $\pi$  and  $\sigma$  components are satisfactory except for the wavelength regions excluded from the fitting. However, with increasing the magnetic field strength, the emission intensity and thus S/N ratio decrease. Consequently, for the case of 7.0 T, the deviation becomes larger. A further detailed comparison is possible by using a higher wavelength resolution system, like the one used in the first experiment, which can resolve peaks in a wavelength range 430.70-430.85 nm. This is a task for the future study.

## 6. Conclusion

The CD  $A^2\Delta - X^2\Pi$  transition spectra under an external magnetic field were calculated by quantum mechanical perturbation method and measured by using glow-discharge plasmas. The values of the equilibrium molecular constants,  $T_e$ ,  $\omega_e$ , and  $B_e$  for the  $A^2\Delta$  state, were determined from the comparison of the calculated and observed spectra without magnetic field. The calculated spectra using these values well represent the experimental ones under a magnetic field strength up to 4.0 T. It is therefore feasible to perform the detailed modeling of the shape of the spectrum under an external magnetic field relevant to fusion oriented devices.

## Acknowledgments

This work was supported in part by the Grant-in-Aid for Young Scientists (B) No.22740362 from JSPS.

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## Figure and Table captions

Tab. 1

The equilibrium molecular constants related to the ro-vibronic energies for the CD  $A^2\Delta$  state. The values are given in  $\text{cm}^{-1}$ . The indices give the power of 10 by which the values must be multiplied. The values in the parentheses represent one standard deviation in units of the last quoted digit. (\*The value is cited from [11].)

Fig. 1

A schematic drawing of the experimental apparatuses. PSO stands for the polarization separation optics.

Fig. 2

Measured (the first experiment) and calculated  $Q$ -branch spectra of the CD  $A^2\Delta - X^2\Pi$  transition without an external magnetic field. The lines with markers denote the observed spectra, dashed lines denote the calculated results, horizontal bars shown at the abscissas denote the excluded wavelength regions from the fitting, and vertical ticks indicate the wavelengths of the CD and  $D_2$  transitions.

Fig. 3

Measured (the second experiment) and calculated  $Q$ -branch spectra of the CD  $A^2\Delta - X^2\Pi$  transition. (a) 0.0 T, (b) and (c)  $\pi$  and  $\sigma$  components, respectively, measured under magnetic field strengths of 1.5, 4.0, and 7.0 T. The zero levels of the spectra for 4.0 and 7.0 T are shifted vertically.

| equilibrium<br>molecular constants | values<br>(scaled from CH[12]) | values<br>(present work) |
|------------------------------------|--------------------------------|--------------------------|
| $T_e$                              | 23184.4*                       | 23184.23 (1)             |
| $\omega_e$                         | 2139.6195                      | 2139.651 (7)             |
| $\omega_e x_e$                     | 43.8824                        |                          |
| $\omega_e y_e$                     | -1.34107                       |                          |
| $B_e$                              | 8.03236                        | 8.02848 (8)              |
| $\alpha_e$                         | $2.5150^{-1}$                  |                          |
| $\gamma_e$                         | $-2.86^{-3}$                   |                          |
| $\epsilon_e$                       | $-8.625^{-4}$                  |                          |
| $D_e$                              | $4.4750^{-4}$                  |                          |
| $\beta_e$                          | $1.37^{-5}$                    |                          |
| $\delta_e$                         | $-4.39^{-6}$                   |                          |
| $\zeta_e$                          | $1.06^{-6}$                    |                          |

Table 1: Shikama

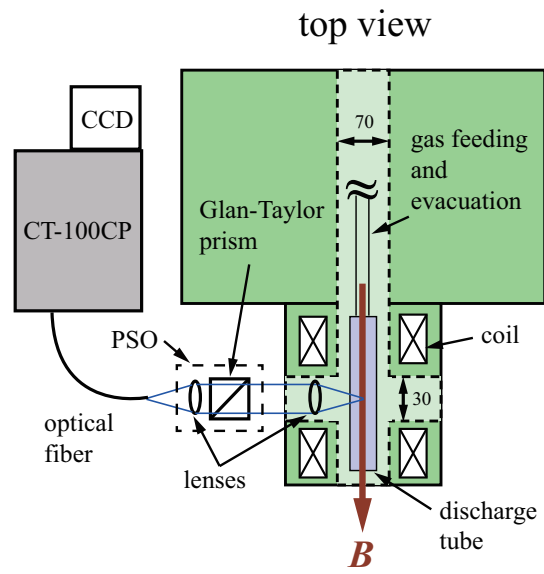


Figure 1: Shikama

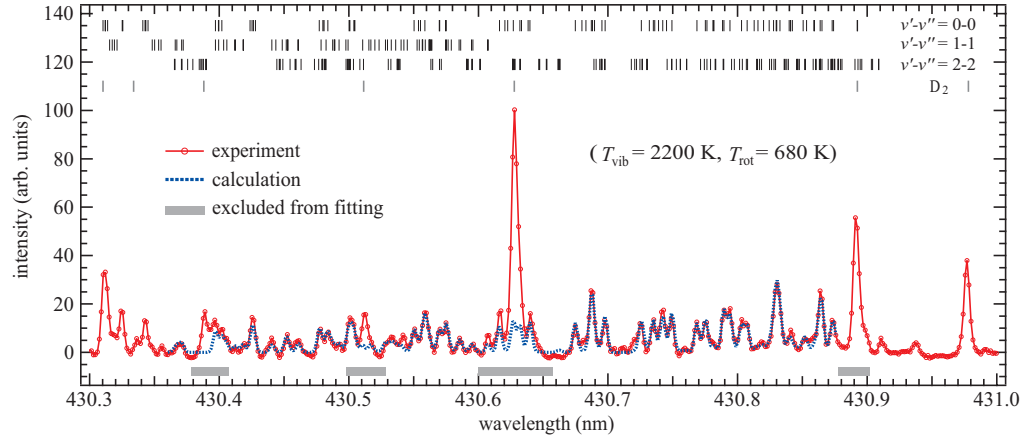


Figure 2: Shikama

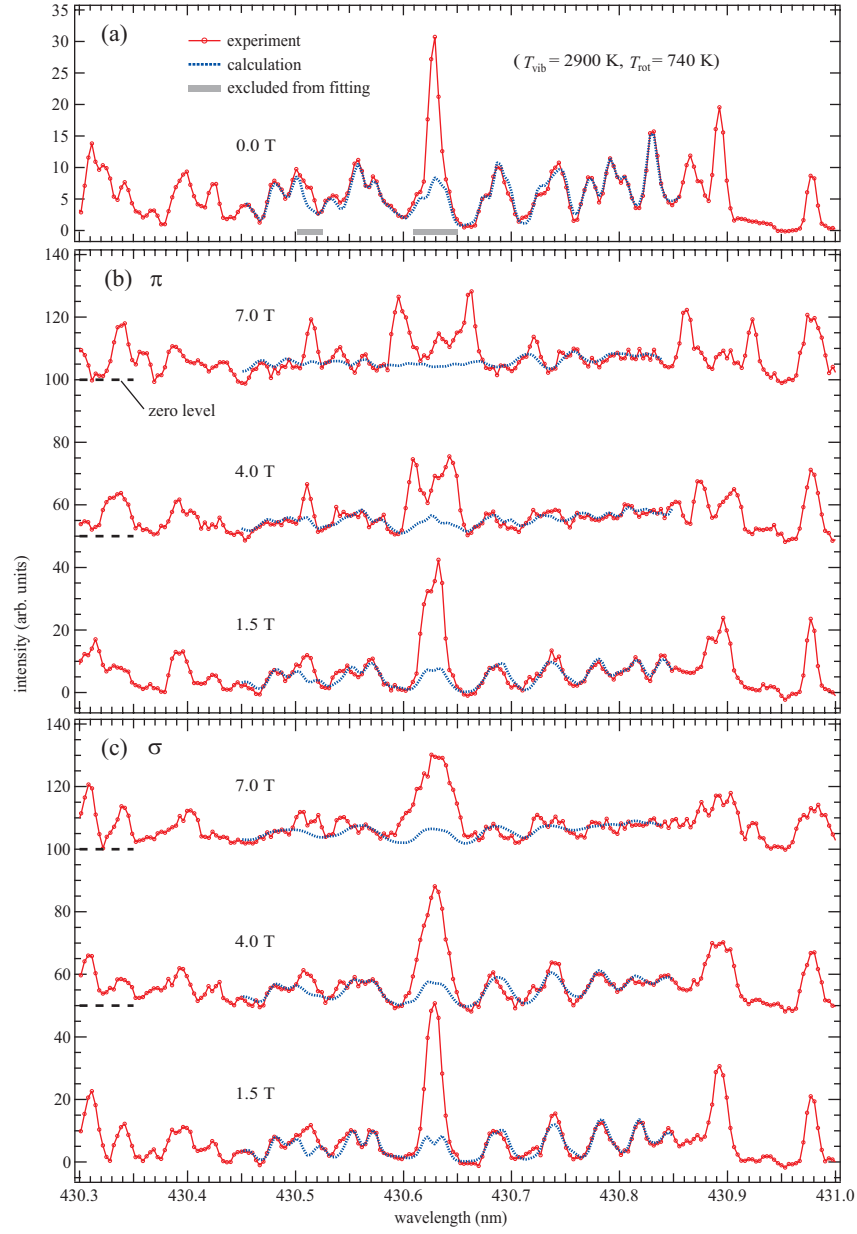


Figure 3: Shikama